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PSI

E-MRS European Materials Research Society

Wir schaffen Wissen – heute für morgen

Radiation grafted polymer electrolyte membranes for water electrolysis cells - Characterization of key membrane properties

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E-MRS Spring Meeting 2014, Symposium CC

Lille, France, 28 May 2014

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Acknowledgements

NOVEL Novel materials and system designs for low cost, efficient and durable PEM electrolysers

New Energy World JTI
fuel cells & hydrogen for sustainability

SINTEF

SEVENTH FRAMEWORK PROGRAMME

Johnson Matthey Fuel Cells
the power within

Innovation in Motion Miba

cea

ETH Zürich

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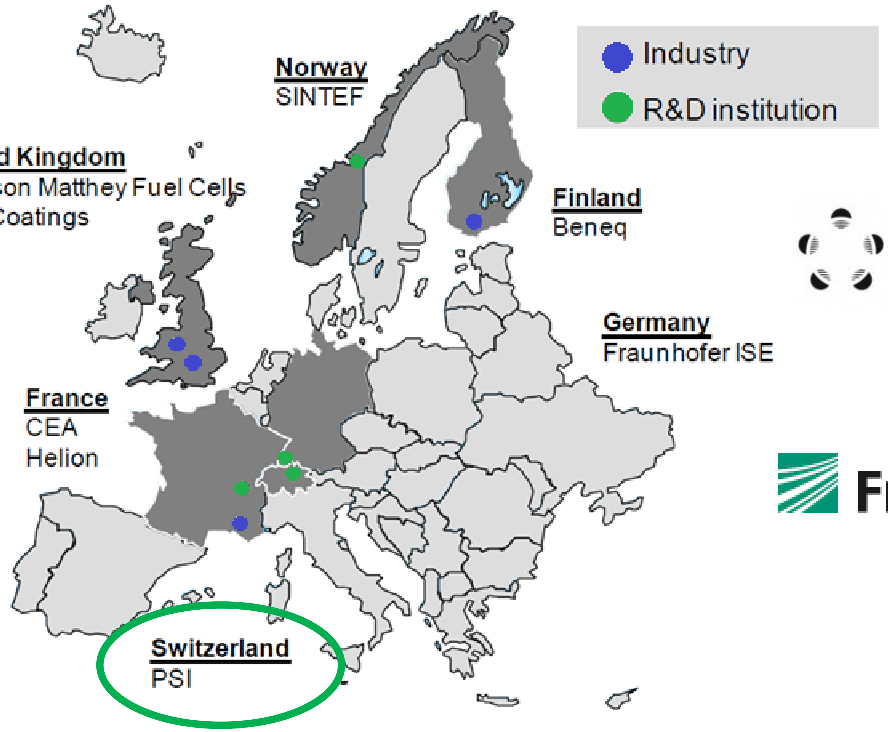

Beneq

Fraunhofer ISE

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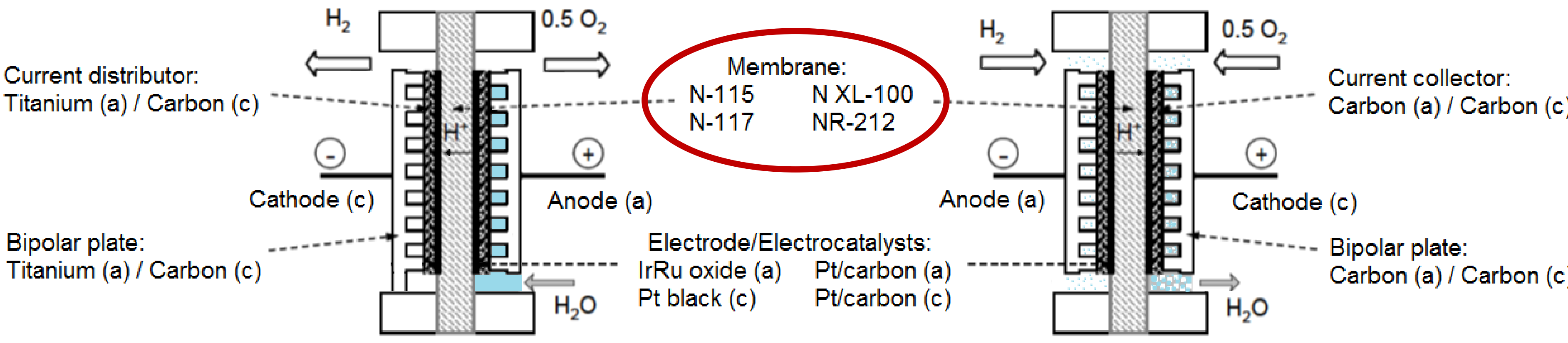
Polymer Electrolyte Electrolyzer vs Fuel Cell

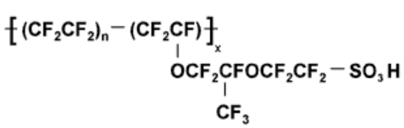
Electrolyzer | Fuel Cell

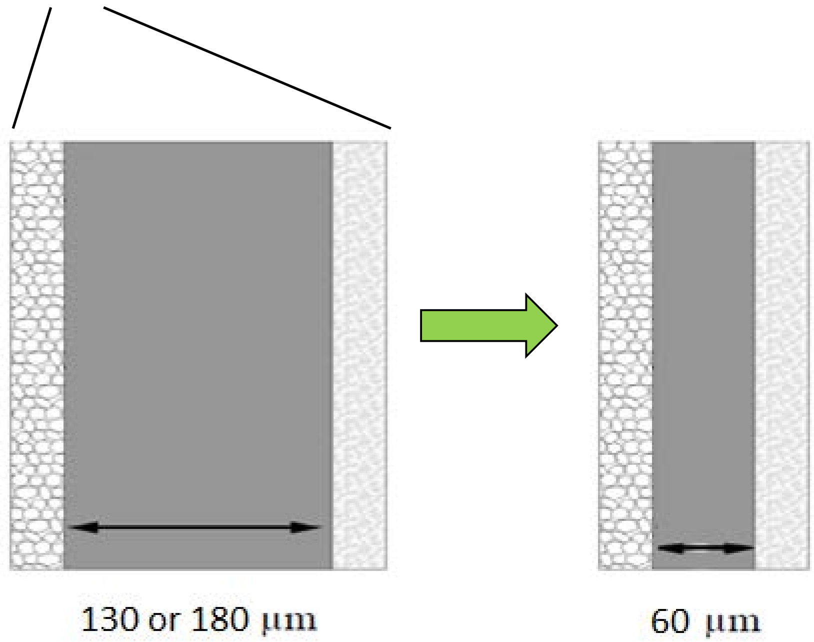


N-115 or N-117

Expensive*

Crossover problem**



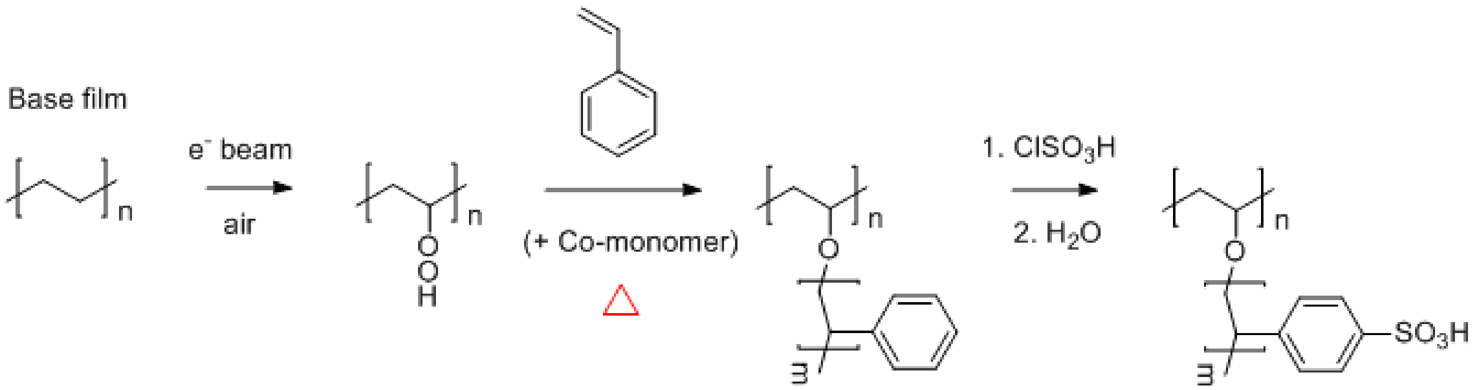


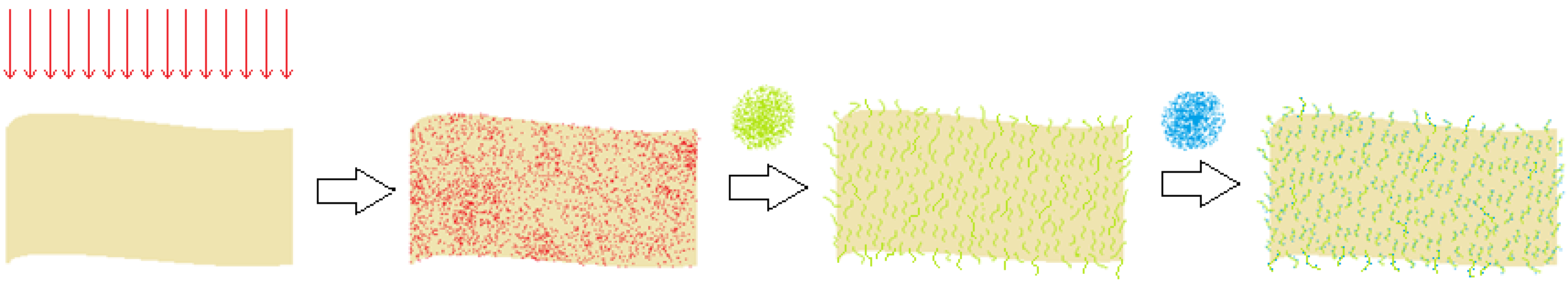
Radiation grafted membrane

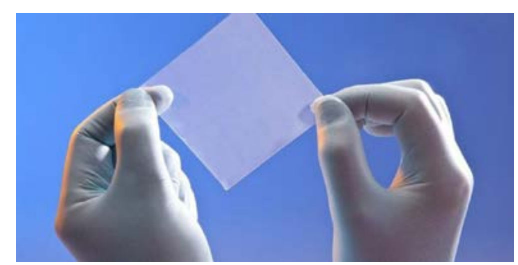
Potentially low cost*

Radiation grafted membrane

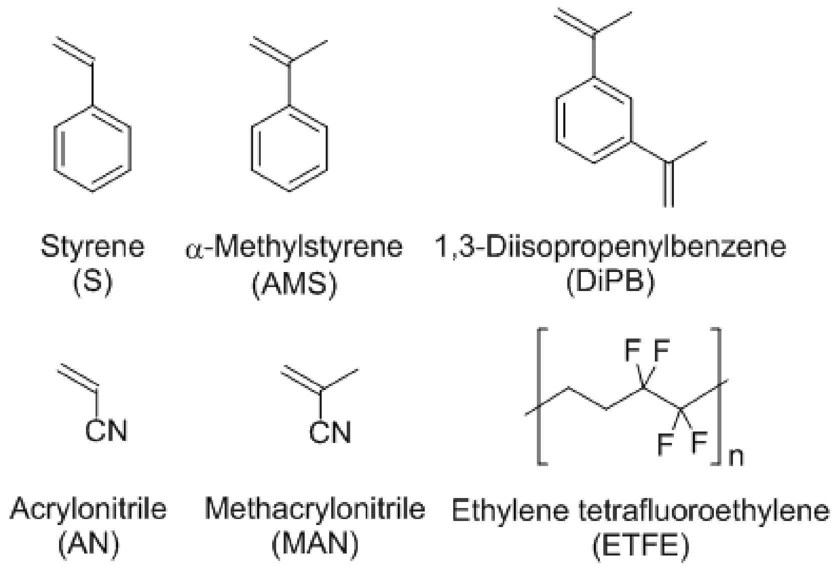
1. Irradiation   2. Polymerisation   3. Sulfonation







Monomers for radiation grafted membrane



	In this research:	Previous work in our group*:
Monomer/co-monomer	<u>S/AN and S/AN/DiPB</u>	AMS/MAN/DiPB (PSI Generation 2)
Base film	<u>ETFE 50 µm base film</u>	ETFE 25 µm base film
Base film supplier	DuPont (D) Saint-Gobain (SG)	DuPont (D) Saint-Gobain (SG)
Application	For electrolyzer	For fuel cell

* L. Gubler, L. Bonorand, ECS Trans. 58, 149 (2013)

Key membrane properties

ASTM: American Society for Testing and Materials

Apply fuel cell technology to characterize membranes for electrolyzer
(same mechanism of proton conduction)

Relative humidity 100%

- Gas barrier property*
  - Gas purity
  - Safety
  - Current efficiency
  - High pressure application
  - → Hydrogen crossover experiment (Electrochemical; Fuel cell; H_2/N_2)
- Resistance*
  - Voltage efficiency
  - → High frequency resistance vs current density (Fuel cell; H_2/O_2)
- Mechanical property
  - Durability
  - High pressure application
  - → Tensile tests (ASTM D882)
- Cost
  - Production
  - → Cost estimation**

* M. Schalenbach, M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, Int J Hydrog Energy 38, 14921 (2013) ** L. Gubler, L. Bonorand, ECS Trans. 58, 149 (2013)

Gas crossover and resistance

S: Styrene ; AN: Acrylonitrile ; DiPB: 1.3-Diisopropenylbenzene
AMS: α-Methylstyrene ; MAN: Methacrylonitrile

Property map

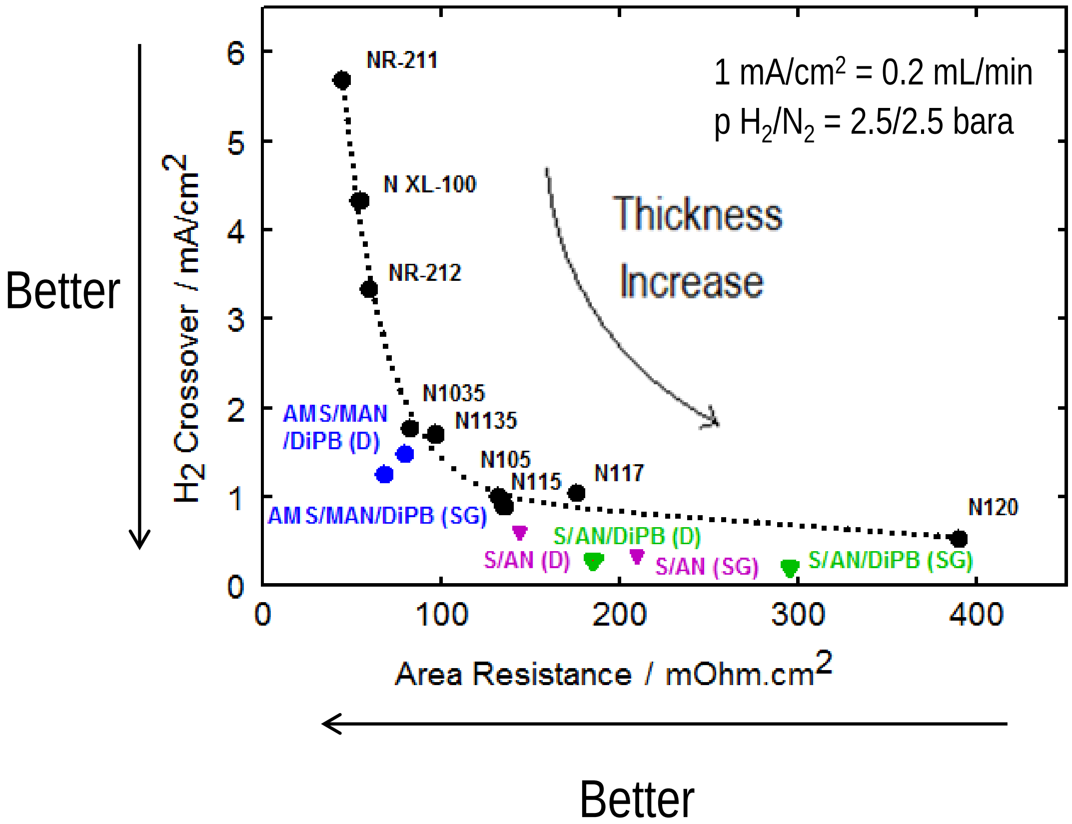
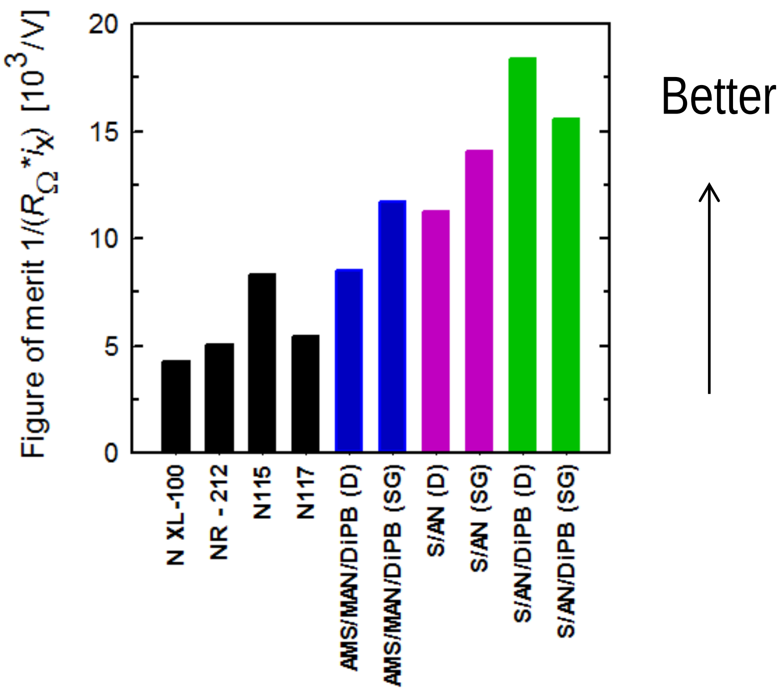


Figure of merit (M)



$$M = \frac{1}{R_\Omega \cdot i_x}$$

- S/AN and S/AN/DiPB: better gas barrier property
- Similar resistance to N-115 or N-117

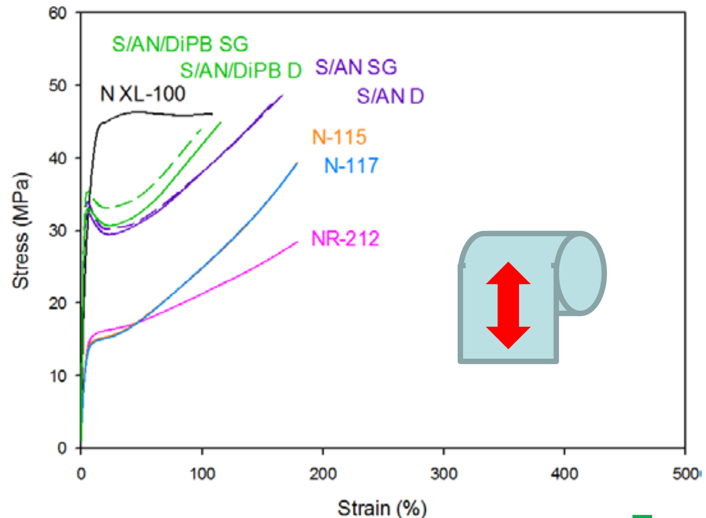
M : Figure of merit (V)
R_Ω: Area resistance (mΩ·cm²)
I_x : Gas crossover current density (mA/cm²)

D: DuPont base film; SG: Saint-Gobain base film

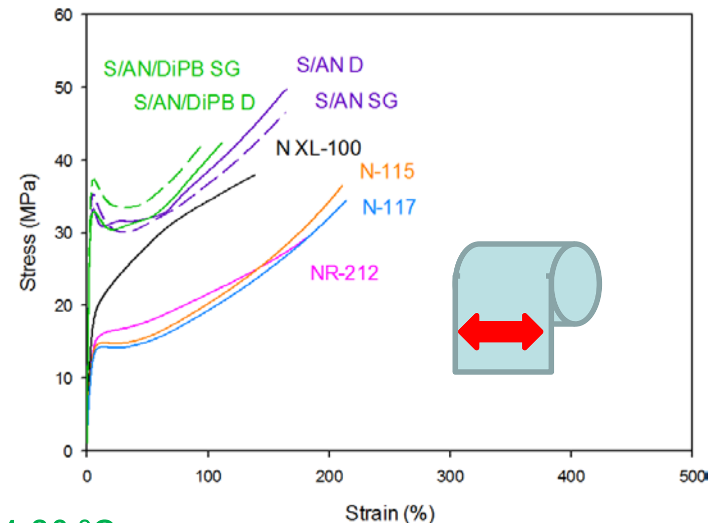
Mechanical property

S: Styrene ; AN: Acrylonitrile ; DiPB: 1.3-Diisopropenylbenzene
AMS: α-Methylstyrene ; MAN: Methacrylonitrile

Tensile Test in Machine Direction
(Ambient condition)

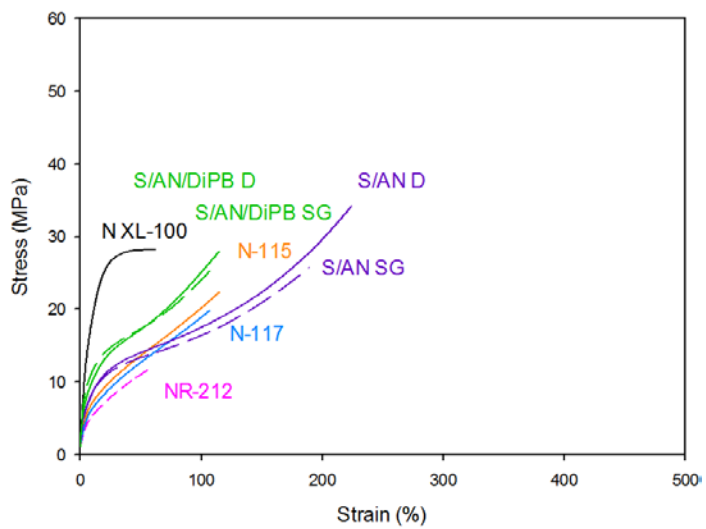


Tensile Test in Transverse Direction
(Ambient condition)

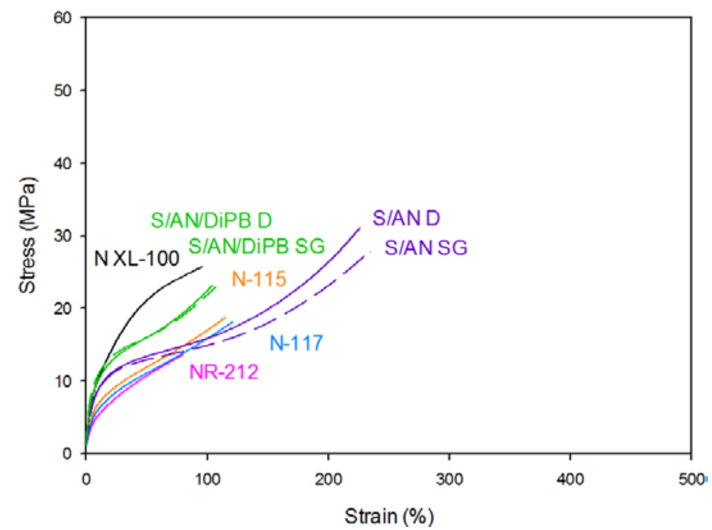


Temperature: 24-26 ^{o}C
Humidity: 25-35 %

Tensile Test in Machine Direction
(Fully hydrated condition)



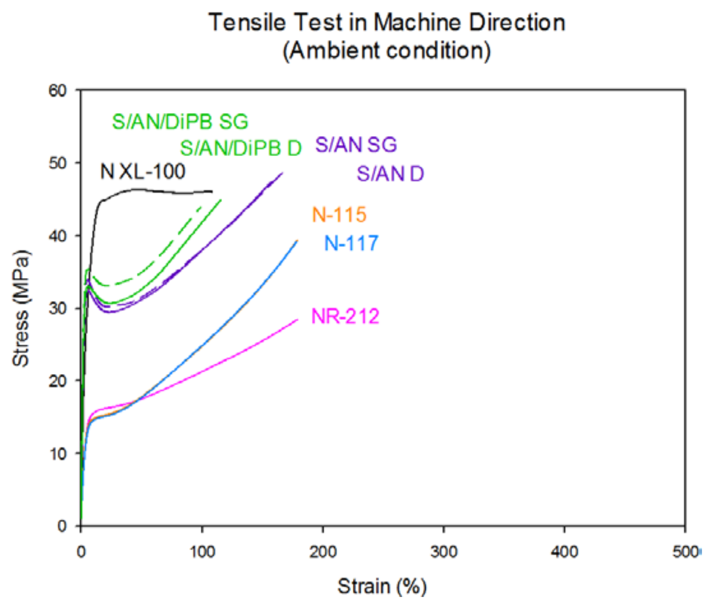
Tensile Test in Transverse Direction
(Fully hydrated condition)

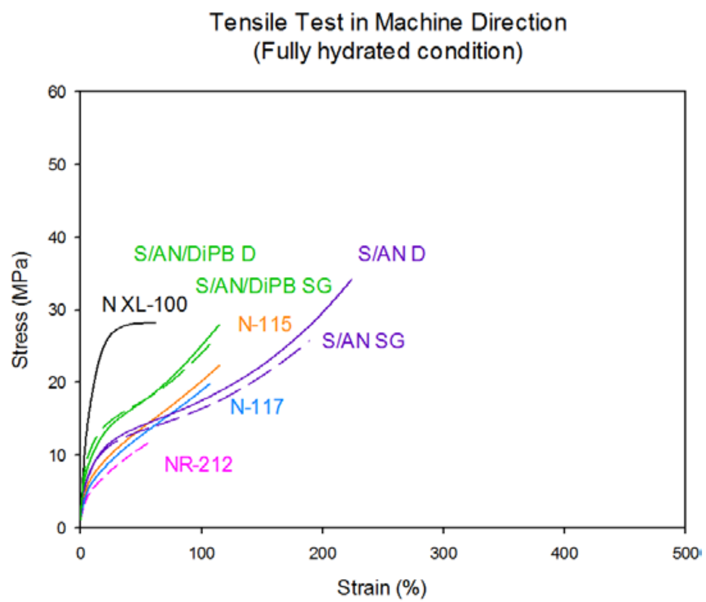


D: DuPont base film; SG: Saint-Gobain base film

Mechanical property

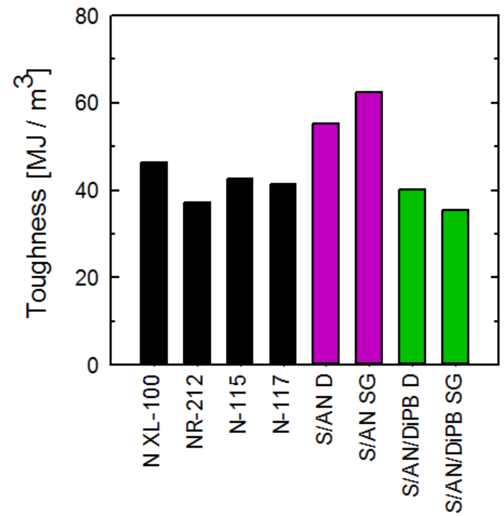
S: Styrene ; AN: Acrylonitrile ; DiPB: 1.3-Diisopropenylbenzene
AMS: α-Methylstyrene ; MAN: Methacrylonitrile



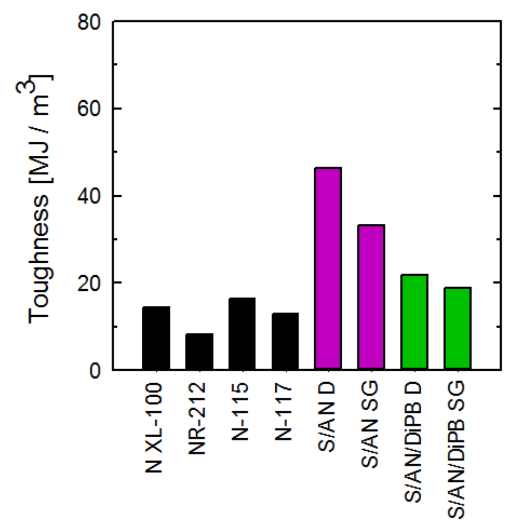


Tensile Energy to Break / Toughness
[MJ / m^3 or Mpa]

Ambient condition (Machine direction)



Fully hydrated condition (Machine direction)



D: DuPont base film; SG: Saint-Gobain base film

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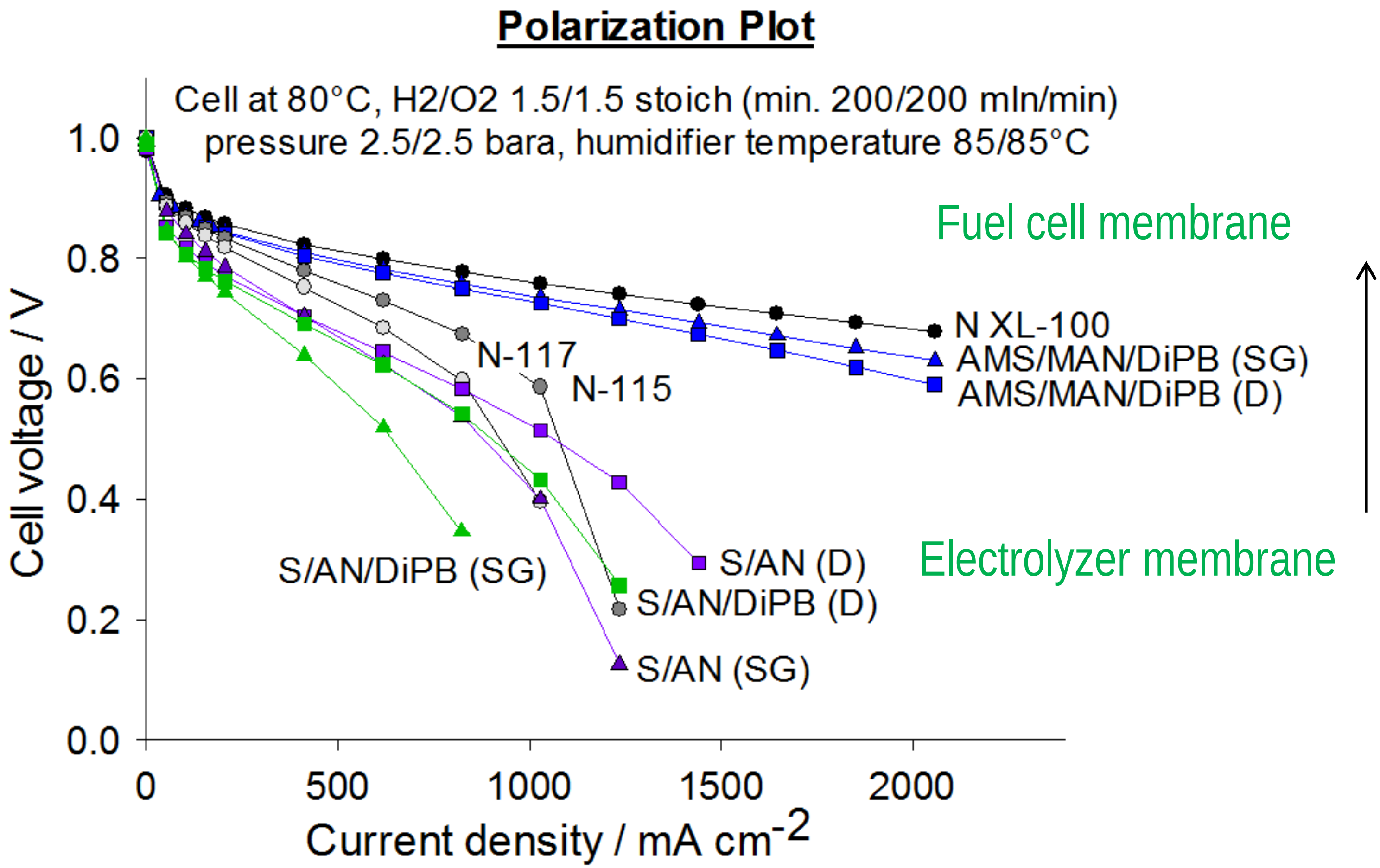
Fuel Cell Performance

S: Styrene ; AN: Acrylonitrile ; DiPB: 1.3-Diisopropenylbenzene
AMS: α-Methylstyrene ; MAN: Methacrylonitrile



Membrane performance trend in fuel cell = performance trend in electrolyzer
theoretically yes, in reality ???

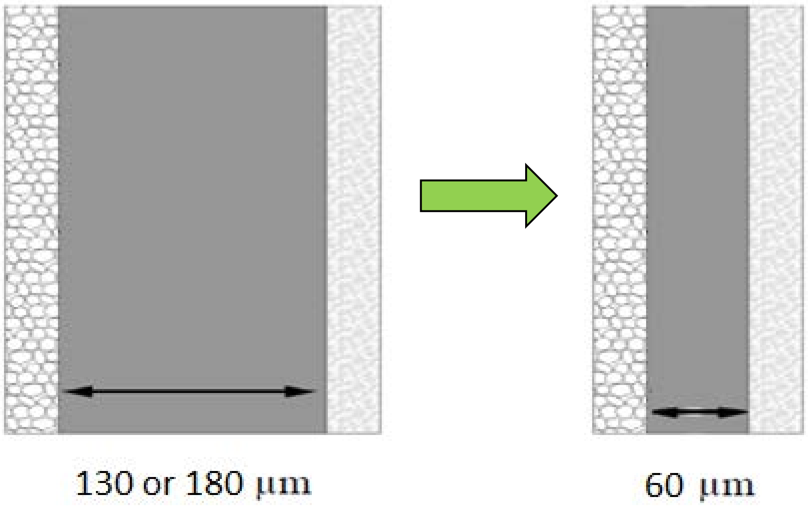
Validation in electrolyzer will be done.

D: DuPont base film; SG: Saint-Gobain base film

Summary

S: Styrene ; AN: Acrylonitrile ; DiPB: 1.3-Diisopropenylbenzene
AMS: α-Methylstyrene ; MAN: Methacrylonitrile

N-115 or N-117 S/AN and S/AN/DiPB membranes



- Better gas barrier property
- Similar resistance
- Better mechanical property
- Lower cell performance (can be improved)
- Potentially low cost*

➢ Promising alternatives membranes

* L. Gubler, L. Bonorand, ECS Trans. 58, 149 (2013)

Electrochemistry Laboratory

Electrochemistry Laboratory Head and Section Head
Prof. Dr. Thomas J. Schmidt

Membrane and Electrochemical Cells Group Leader
Dr. Lorenz Gubler

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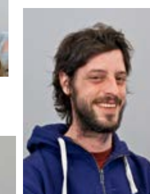
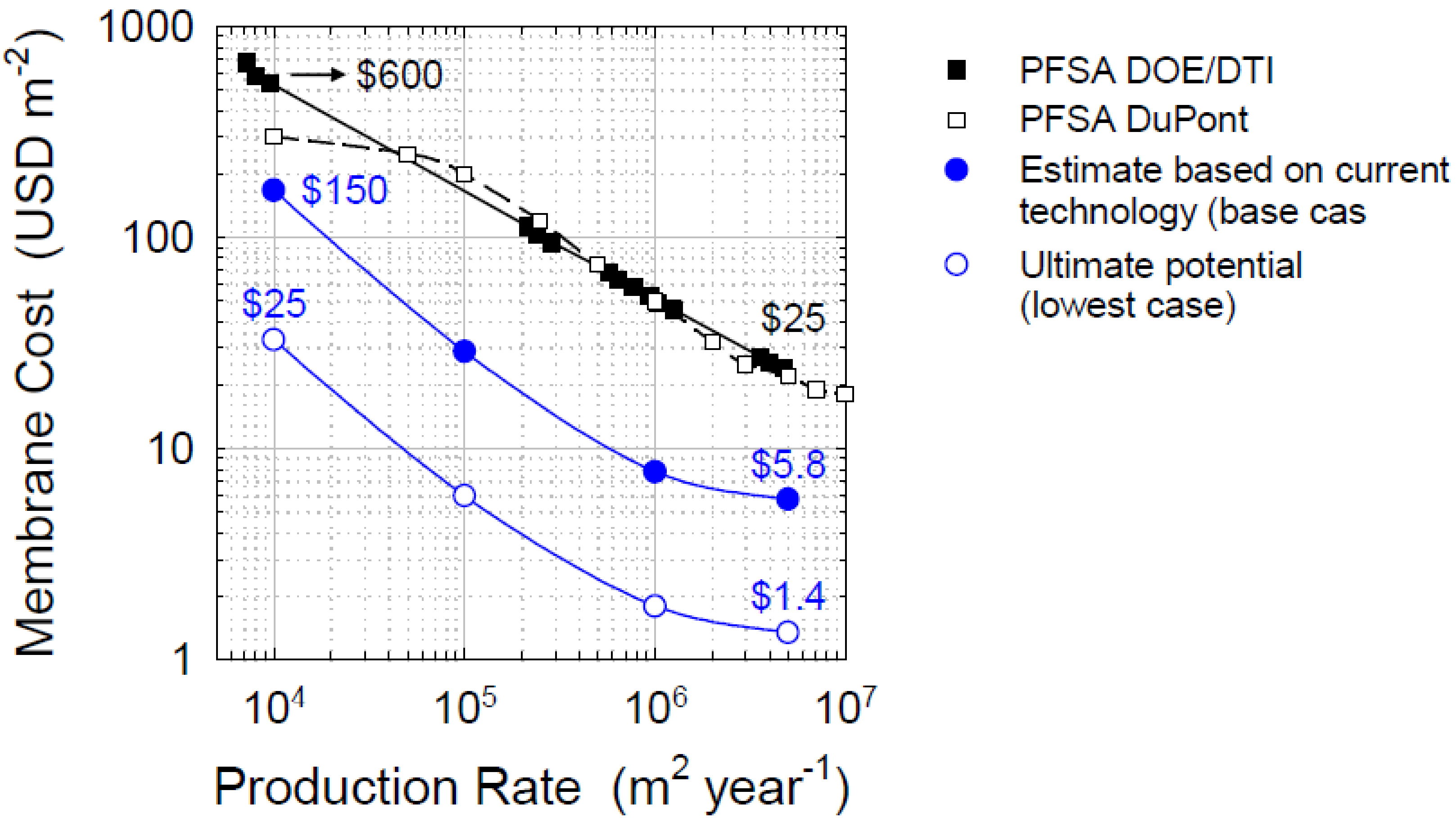
  - Jürg Thut
- **Postdoc**
  - Dr. Maria Georgmezi
- **PhDs**
  - Yves Buchmüller
  - Zhang Zhuoxiang
  - Tom Engl
  - Joanna Conder
  - Albert Albert
  - Véronique Sproll
  - Olga Nibel



Back Up Slides

Estimated cost of production of membranes*



* L. Gubler, L. Bonorand, ECS Trans. 58, 149 (2013)

Experiment

Fuel cell condition:

Single cell with 30 cm^2 active area; cell temperature 80 ºC

Gas diffusion electrode JM ELE0162, 0.4 mg Pt/cm^2; hot-pressed at 120 °C

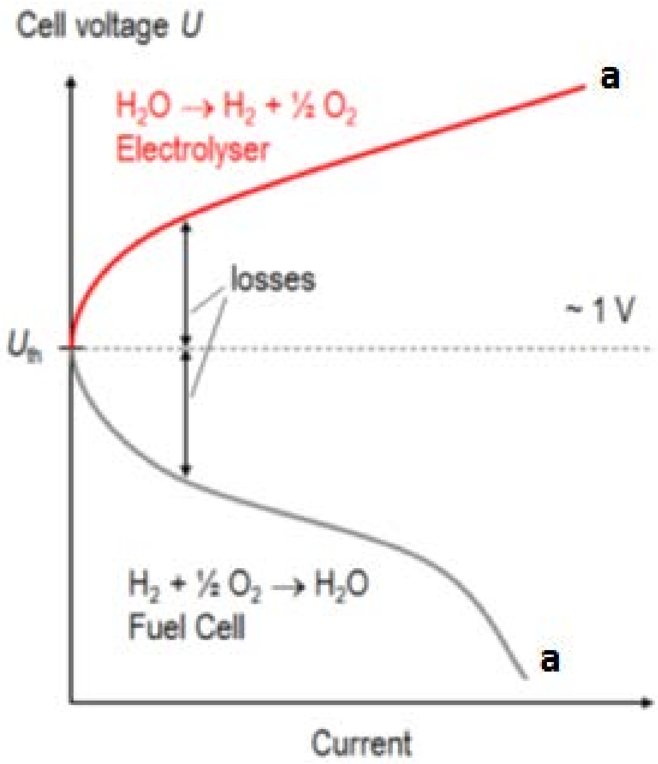
H_2/O_2 (N_2); 1.5/1.5 stoichiometrie

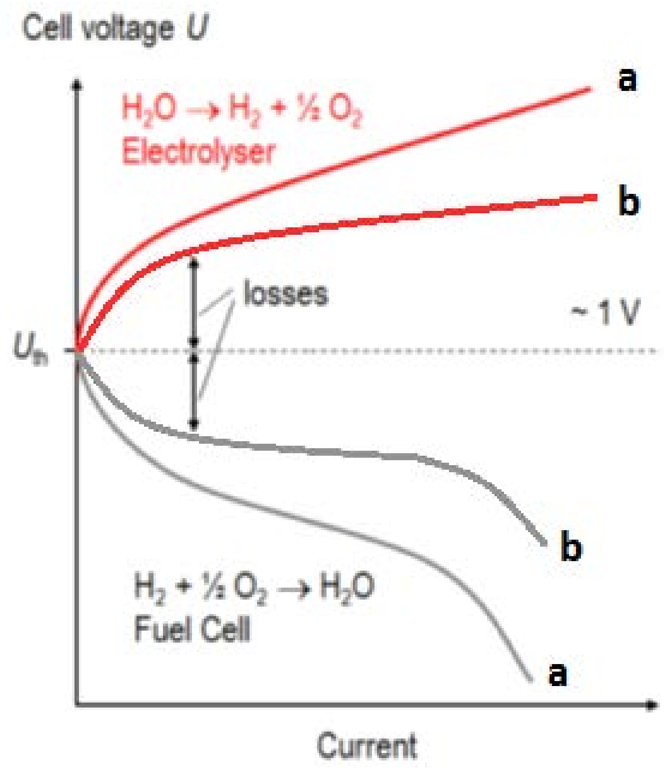
Minimal flow 200/200 mln/min

Pressure 2.5/2.5 bar absolute

Relative humidity 100% (Humidifier temperature 85/85 ºC)

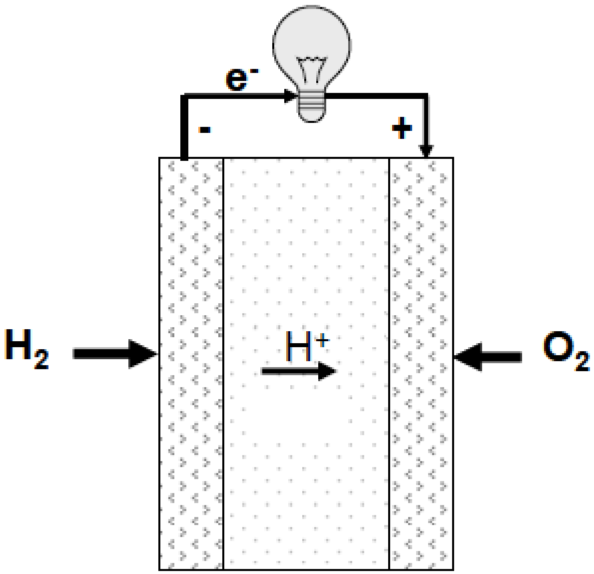
Electrolyzer vs Fuel Cell

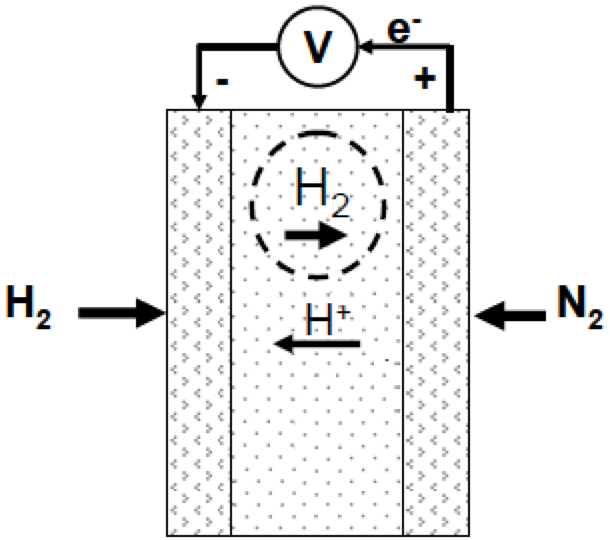




How to measure gas crossover ?

	Normal Fuel Cell Operation	*Crossover Experiment*
(−)	$H_2 \rightarrow 2H^+ + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
(+)	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$H_2 \rightarrow 2H^+ + 2e^-$



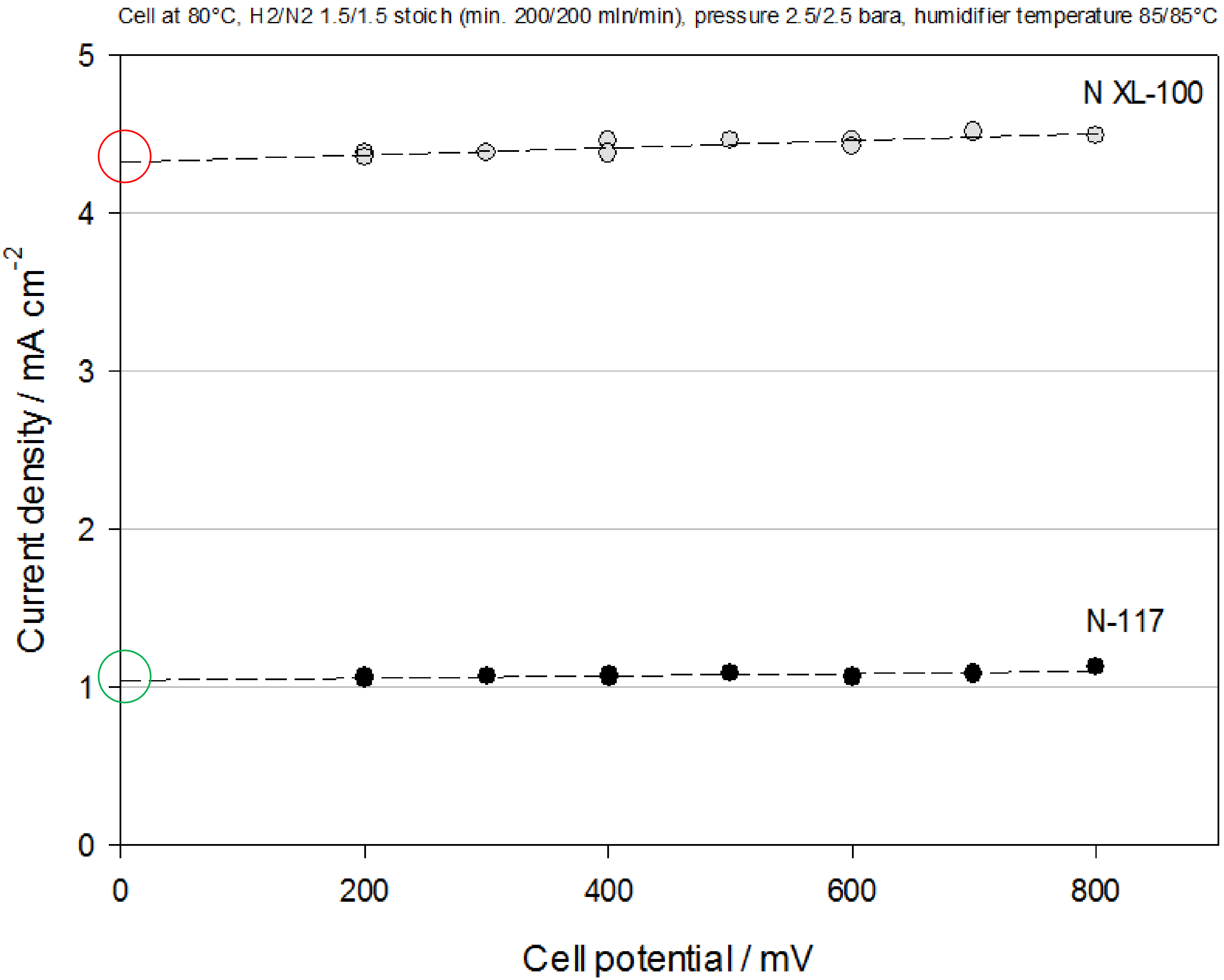


Potential is set.

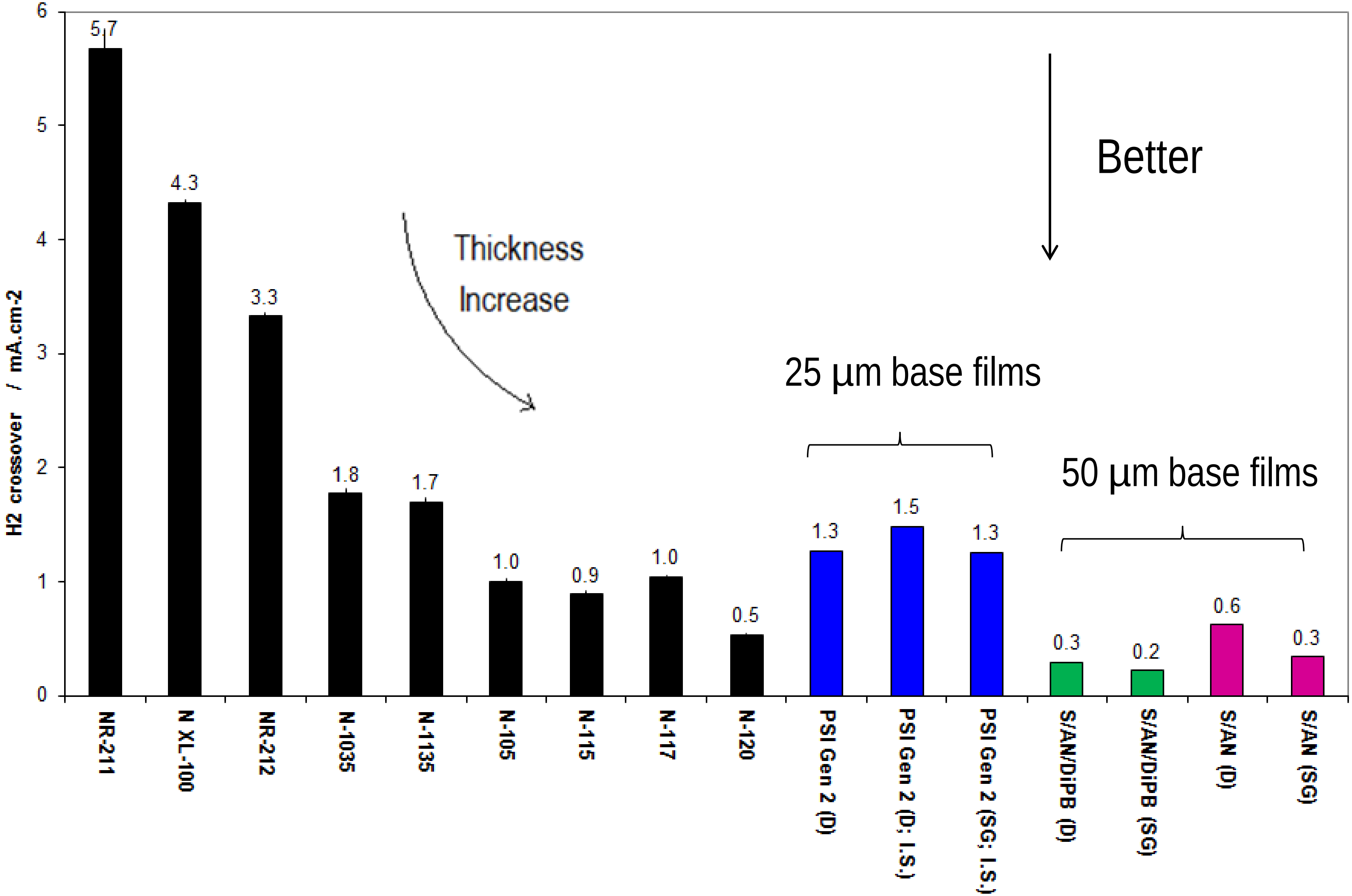
Current density is measured.

Gas crossover current densities

Hydrogen Permeation

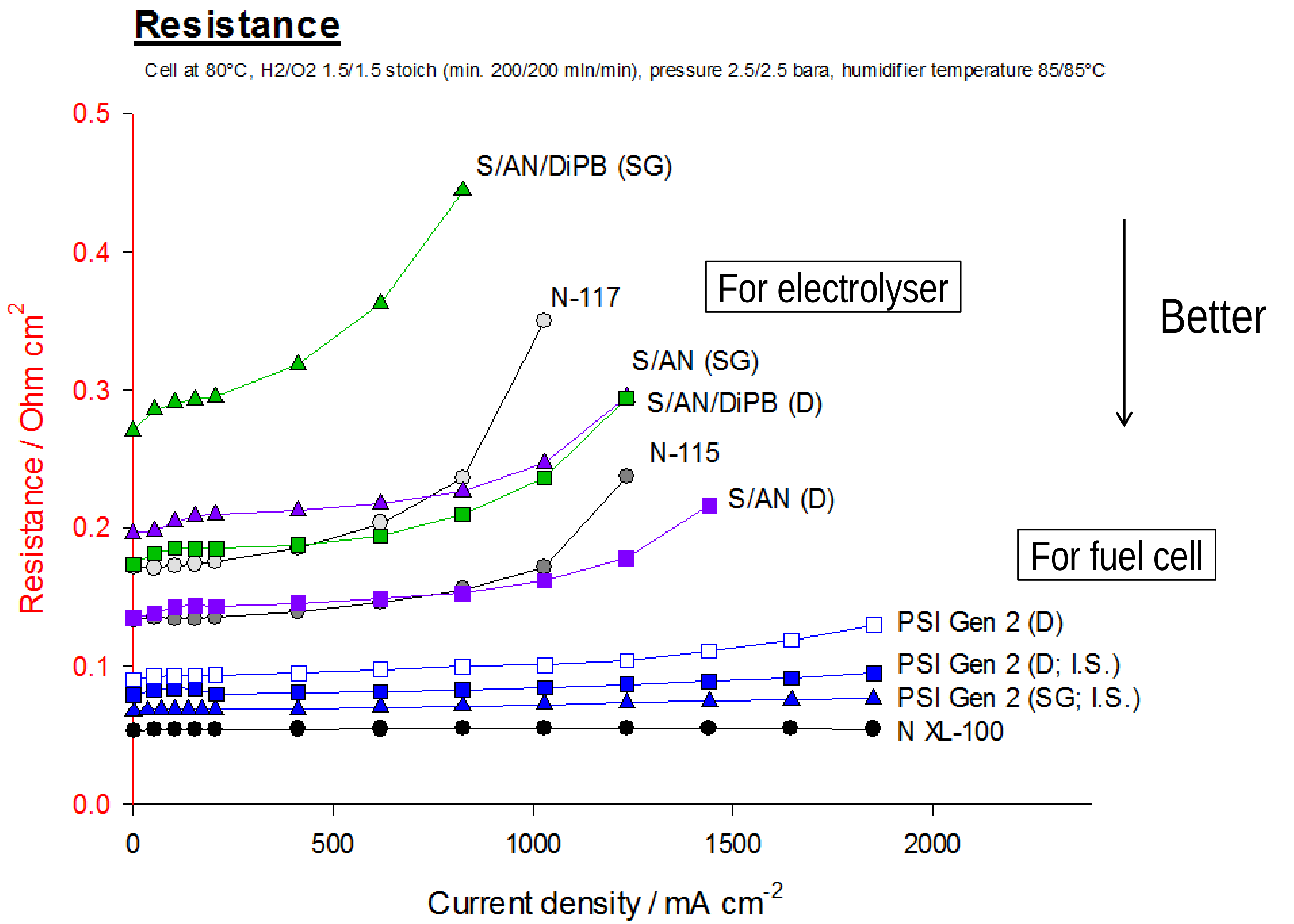


Gas crossover current densities



D: DuPont base film; SG: Saint-Gobain base film; I.S.: improved surface

Resistance



D: DuPont base film; SG: Saint-Gobain base film; I.S.: improved surface

Mechanical Testing (ambient condition)

Membrane	Machine Direction			Transverse Direction		
	Thickness (µm)	Tensile strength (MPa)	Elongation at Break (%)	Thickness (µm)	Tensile strength (MPa)	Elongation at Break (%)
NR-211	24.8 ± 0.4	27.6 ± 0.6	149.1 ± 4.5	24.4 ± 0.2	27.8 ± 0.6	146.8 ± 4.7
N XL-100	27.2 ± 0.3	45.0 ± 1.1	105.6 ± 9.9	27.0 ± 0.5	38.5 ± 1.1	135.6 ± 8.1
NR-212	50.0 ± 0.5	28.8 ± 0.9	178.4 ± 8.4	51.5 ± 0.4	29.8 ± 1.5	185.5 ± 11.9
N-1035	71.3 ± 1.8	41.8 ± 1.8	101.2 ± 5.3	75.0 ± 1.7	33.2 ± 1.5	171.9 ± 4.4
N-1135	80.2 ± 1.4	40.2 ± 2.3	123.8 ± 10.4	82.1 ± 1.0	33.5 ± 1.4	203.0 ± 8.6
N-105	127.6 ± 1.8	38.9 ± 2.3	143.3 ± 5.1	125.9 ± 1.2	30.0 ± 1.1	216.9 ± 8.4
N-115	137.3 ± 1.6	39.3 ± 0.6	178.0 ± 3.2	134.5 ± 1.7	35.2 ± 1.7	207.8 ± 7.2
N-117	183.6 ± 2.7	38.2 ± 2.5	174.7 ± 10.5	173.6 ± 8.6	34.5 ± 1.8	214.0 ± 8.7
N-120	264.8 ± 1.9	38.5 ± 0.9	216.9 ± 7.5	261.8 ± 4.2	35.3 ± 1.8	245.9 ± 11.3
ETFE 50 µm D	49.6 ± 0.7	58.0 ± 3.3	343.5 ± 14.6	52.9 ± 0.7	51.7 ± 3.2	358.1 ± 21.0
ETFE 50 µm SG	51.4 ± 1.2	53.1 ± 2.2	333.8 ± 15.8	51.7 ± 0.7	52.2 ± 3.3	414.8 ± 21.5
S/AN D	62.2 ± 1.6	46.9 ± 1.8	154.2 ± 10.6	62.3 ± 2.3	48.4 ± 2.6	166.5 ± 12.7
S/AN SG	62.6 ± 0.7	49.7 ± 2.1	165.3 ± 12.0	66.0 ± 0.6	47.2 ± 1.2	165.8 ± 8.3
S/AN/DiPB D	66.4 ± 0.8	44.6 ± 1.1	115.1 ± 6.2	68.0 ± 0.7	43.0 ± 0.6	111.8 ± 2.1
S/AN/DiPB SG	69.6 ± 1.1	43.7 ± 1.0	98.5 ± 2.7	70.3 ± 0.7	41.9 ± 0.6	92.5 ± 6.6

Mechanical Testing (fully hydrated condition)

Membrane	Machine Direction			Transverse Direction		
	Thickness (µm)	Tensile strength (MPa)	Elongation at Break (%)	Thickness (µm)	Tensile strength (MPa)	Elongation at Break (%)
NR-211	29.4 ± 0.3	12.9 ± 1.7	62.7 ± 16.0	29.2 ± 0.2	13.8 ± 2.1	69.5 ± 20.5
N XL-100	35.8 ± 0.4	26.6 ± 2.2	61.9 ± 28.0	36.1 ± 0.3	25.5 ± 1.3	96.3 ± 18.4
NR-212	63.4 ± 0.7	13.3 ± 5.1	77.3 ± 50.0	63.8 ± 0.9	12.8 ± 3.4	72.1 ± 34.0
N-1035	109.6 ± 2.8	19.8 ± 2.8	84.2 ± 15.1	108.5 ± 5.8	16.1 ± 2.1	117.9 ± 19.6
N-1135	101.2 ± 2.2	21.1 ± 1.2	93.5 ± 8.4	102.0 ± 2.4	17.4 ± 2.0	121.4 ± 19.0
N-105	143.0 ± 1.9	23.6 ± 1.5	115.9 ± 9.0	140.5 ± 2.2	18.5 ± 1.2	140.6 ± 9.8
N-115	149.6 ± 3.8	22.3 ± 1.5	114.7 ± 9.2	151.4 ± 1.8	18.5 ± 2.4	111.8 ± 20.6
N-117	195.0 ± 3.6	19.2 ± 3.0	101.5 ± 22.7	197.7 ± 8.6	18.2 ± 3.1	119.4 ± 28.3
N-120	294.5 ± 4.4	21.8 ± 2.2	137.3 ± 21.5	290.1 ± 2.2	21.2 ± 0.6	160.5 ± 6.6
S/AN D	86.5 ± 2.4	33.8 ± 4.7	225.9 ± 22.9	84.6 ± 3.1	31.1 ± 2.8	226.7 ± 16.1
S/AN SG	85.3 ± 3.5	27.0 ± 4.1	189.1 ± 30.5	90.1 ± 1.7	26.5 ± 6.7	212.8 ± 54.8
S/AN/DiPB D	73.7 ± 3.7	28.1 ± 2.1	116.9 ± 11.4	78.0 ± 1.3	22.8 ± 3.5	101.1 ± 24.4
S/AN/DiPB SG	82.7 ± 1.6	25.3 ± 3.0	106.6 ± 18.3	82.2 ± 2.2	22.7 ± 2.4	106.2 ± 17.9